Quality Assurance Project Plan
for
Real-Time, Continuous Monitoring of Bromide and Nutrients at H.O. Banks Pumping Plant and San Joaquin River near Vernalis.

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California Department of Water Resources
Division of Environmental Services
Municipal Water Quality Investigations Program
Post Office Box 842836
Sacramento, California 94236-0001
Contract Number: 4600001642

Department of Water Resources
Project Managers

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3. Distribution List

The following individuals and organizations have received copies of the approved Quality Assurance Project Plan:

Dan Otis	Department of Water Resources
Cindy Messer	Department of Water Resources
David Gonzalez	Department of Water Resources
Frances Brewster	Santa Clara Valley Water District
Paula Trigueros	San Francisco Estuary Project
Sam Harader	CALFED

4. Project Organization

The Real Time, Continuous Monitoring of Bromide and Nutrients at H.O. Banks Pumping Plant and San Joaquin River near Vernalis Project is a CALFED-funded project that is being conducted by the California Department of Water Resources (DWR), Municipal Water Quality Investigations Unit (MWQI) under a subcontract between Santa Clara Valley Water District and DWR. Table 1 lists the key DWR personnel responsible for the project.

Table 1. Project organization structure

Title/responsibility	Name	Phone number
Project managers	Jaclyn Pimental	(916) 651-9686
	David Gonzalez	(916) 371-3163
Staff	Steven San Julian	(916) 371-2284
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5. Problem Identification/Background

Waters of the Sacramento-San Joaquin Delta serve nearly 23 million people living in the San Francisco Bay-Delta region and in Southern California. Therefore, maintaining good water quality in the Delta is important to public health and the economy of the state. Anions in Delta waters, especially bromide, are a growing concern for drinking water quality. The primary sources of bromide in the State Water Project (SWP) are seawater intrusion and agricultural return water from within the Delta and along the San Joaquin River. During low Delta inflow periods, seawater sources dominate bromide loads in the SWP. The bromide load in the San Joaquin River is derived from the recirculation of salts from agricultural irrigation return water. CALFED has also identified nutrients as drinking water parameters of concern. Nutrients such as nitrate and phosphate can enhance nuisance algae blooms that affect water filtration and cause low dissolved oxygen levels due to microbial decomposition of dead algae and phytoplankton.

Fluctuating source water quality and more stringent regulatory requirements make it more challenging for water utilities to provide safe, reliable, and economical drinking water. Water utilities are strictly regulated with respect to the formation of disinfection byproducts. The disinfection byproducts of greatest concern for Delta water users are total trihalomethanes (TTHM) and bromate. Bromide concentration in source water is a key factor in the formation of these byproducts.

In order to better monitor fluctuations in Delta water quality, CALFED has provided funding for three real-time organic carbon analyzers installed at the Harvey O. Banks Pumping Plant (Banks PP), on the Sacramento River at Hood, and on the San Joaquin River near Vernalis. These organic carbon analyzers are part of the Real Time Data and Forecasting (RTDF) Project that was developed by MWQI. Data from these stations are available on DWR's California Data Exchange Center Web site (cdec.water.ca.gov). The real-time monitoring of anions in the Delta will create a similar system for bromide and nutrient data collection by installing anion analyzers at the Banks P.P. and the San Joaquin River near Vernalis stations.

Access to real-time bromide data will allow water agencies to make source water and treatment changes based on bromide concentrations. Through the use of real-time data, high

bromide levels can be anticipated, and operational changes such as reducing pre-chlorination or blending sources can be made to lower THM formation.

Anion data typically have been collected as grab samples for laboratory analysis on a weekly or monthly basis. This frequency of data has proven to be of limited value in establishing baseline water quality conditions and in assessing concentrations of anions in the system. This project, as an important component of the RTDF project, will develop and implement a monitoring system for anions that can be used in the development of an early-warning/ forecasting system and for developing simulation models to predict movement and concentration of anions in the SWP. This project will provide real-time data on selected anions in the San Joaquin River and at the headworks of the SWP. The data from this project will be used by the State Water Contractors on a real-time basis as an aid to adjusting water treatment and blending activities.

6. Project/Task Description

Real-time monitoring of selected anions has previously not been conducted in the Delta. The primary objective of this project is to determine the feasibility of establishing field stations for the continuous monitoring of surface water anion levels. The major tasks of the project are:

1. Evaluate current analytical methods and instruments for anion analysis
2. Install and operate anion analyzers at key field locations
3. Evaluate the accuracy of the data generated by the field instruments
4. Evaluate and install a data telemetry system to provide real-time access to anion data and allow for remote operation of the analyzers
5. Determine if long-term operation of these analyzers is logistically feasible

The first task in this project—to review and purchase anion analyzers—has been completed. The criteria used to evaluate potential analyzers included (1) the ability to operate in an unattended mode, (2) telemetry/remote-control capabilities, and (3) the ability to produce laboratory-quality anion measurements under different water quality conditions. After conducting a review of bromide and nutrient instrumentation, staff determined that ion chromatography was the only viable method for real-time, continuous field measurement of these constituents. The chosen instrument was the Dionex DX-800 process analyzer (Dionex Corporation, Sunnyvale, CA). Although several companies build ion chromatography analyzers, Dionex Corporation is the only manufacturer that offers an online, process analyzer that can operate unattended for up to 2 weeks. A minimum 2-week service interval was required to make operation of any online analyzer cost-effective and practical for field crew operations. Normal laboratory anion analyzers are not designed for long-term, unattended operation. Thus, the Dionex DX-800 was the only instrument found suitable at the time for real-time, continuous monitoring of bromide and nutrients in the SWP and San Joaquin River.

The anion analyzers will be installed at 2 locations in the Delta. The locations were selected based on their relative contributions of bromide and other anions of interest to drinking water utilities. The two sites are (1) the Banks P.P. near Byron, California, and (2) the San Joaquin River near Vernalis station. The Banks P.P. was selected due to its location at the head of the SWP. Banks P.P receives a blend of water from the Sacramento and San Joaquin River watersheds and the San Francisco Bay-Delta watershed and is representative of the water flowing to water utilities south of the Delta. The San Joaquin River near Vernalis station was

selected to represent contributions from re-circulated bromide from agricultural runoff in the San Joaquin Valley. In addition, continuous nitrate and phosphate measurements on the San Joaquin River will aid in understanding baseline nutrient loads.

Figure 1. Banks (L) and Vernalis (R) stations

MWQI is already using these sites for discrete and real-time water quality sampling. The Banks P.P. location has an existing instrument shelter that houses a Shimadzu total organic carbon analyzer (TOC) and other DWR equipment. Due to limited space in the existing shelter, a new shelter will be built in order to install the anion analyzer. In July 2004, a Tuff Shed will be built on the site. The Shimadzu TOC analyzer and the Dionex anion analyzer will be housed in this shed, and a new water intake and filtration system will be installed as well as phone lines. The installation of the anion analyzer will begin in January 2005 and continue into Febuary. Dionex field technicians will install the anion analyzer and give introductory instructions to MWQI field staff on the operation of the instrument. Trial operation of the anion analyzer will begin in February 2005 with the focus on methods development and calibration.

A new water quality monitoring station will be built at the San Joaquin River near Vernalis station; it is scheduled to be completed in February 2005. MWQI field staff will install all of the support equipment, including the submersible pump, water intake lines, and filtration system. The installation of the second anion analyzer at this station will begin in April 2005. The sequential installation of the analyzers will allow staff to become familiar with instrument operation and maintenance protocols and transfer this knowledge from one installation to the next. Dionex field technicians will provide some on-site training of MWQI staff; however, additional training in the field of ion chromotagraphy is necessary. Staff will attend Dionex short courses in October 2005 (3 days) on the operation and maintenance of the ion chromatography units. A similar Dionex IC anion analyzer is used at DWR's Bryte Chemical Laboratory (West Sacramento) for routine determination of bromide and other anions in Delta waters. In conjunction with Bryte Laboratory chemists and Dionex field technicians, DWR staff will develop calibration programs and standards that are tailored to meet the specific requirements of both stations.

During the initial months of operation DWR staff will focus on operation and maintence of the analyzers. The analyzers are required to operate continuously in a remote field setting with only weekly or bi-monthly maintenance checks by staff. Evaluation of the analytical systems performance will begin several months after installation and trial operation. In July 2005, DWR

field staff will start to collect grab samples on a weekly to bi-monthly basis for analysis at the Bryte Laboratory. One sample will be collected from the river or canal and one will be collected after the filters at a point along the water supply line. This data will be used to check for nutrient loss or addition within the system. These samples will continue to be collected for as long as the analyzers are in operation. Certified standards from an outside source laboratory will be run on the analyzers on a monthly basis. Testing these standards will provide data for control charts as well as offer information that will assist in defining the precision and accuracy of the Dionex anion analyzers.

The next task will be to configure remote access to the anion analyzers computers. Because of the distance between the office, laboratory, and stations, a reliable data transfer system will be developed in order to manage the analyzers via a remote desktop connection. A frame relay connection will be installed at both the Banks P.P. and Vernalis stations. With remote desktop, staff will be able to remotely start and stop samples, run a calibration, and edit the data. Remote access will also allow staff to transfer and store the data on office computers. The remote desktop connection will be used initially to do daily system and quality checks on the status of the analyzer and sampling results. Data will be obtained using this remote desktop connection by manually exporting and then copying data to a shared network drive. After further evaluation of the analyzers, the data will be made available in a weekly report published by MWQI's RTDF project.

MWQI staff will also create a database to store the anion data and then post the data on the CDEC Web site. The data will be stored in a Micrososft Access database and then be transferred to the CDEC Web site for public access. Development of these data acquisition methods will continue with an emphasis on moving to a completely automated process. The data will be reviewed in the morning. Data considered incorrect due to an error in peak integration or shifting retention times will be corrected or flagged. All data that make it onto the CDEC Web site will be considered preliminary data. Data published on the CDEC Web site and in the RTDF project's weekly report will be used by the State Water Contractors, DWR staff and other users.

Figure 2. Dionex DX-800 Ion Chromatography analyzer at Banks station

6.1 Current Project Status

Because this project is a feasibility study, protocols for routine operation and maintenance of the Dionex analyzers will be continually refined. QA/QC procedures will continue to be developed in order to ensure quality of the data being produced.

A few operational and quality control tasks remain to be completed at both stations. These tasks include completely automating the data transfer, storage, and publication process, continuing to test of certified standards, and completing a final report evaluating the feasibility of real-time monitoring of anions at the Banks and Vernalis stations. The final report will be completed in 2008. This QAPP and the final report will fulfill the subcontract between DWR and Santa Clara Valley Water District for the CALFED grant. These and other ongoing project tasks are shown in Table 2.

Table 2. RTDF project tasks for the Banks and Vernalis stations, 2005–2008

Tasks for Banks and Vernalis real-time stations	Q*1-2005	Q2-2005	Q3-2005	Q4-2005	Q1-2006	Q2-2006	Q3-2006	Q4-2006	Q1-2007	Q2-2007	Q3-2007	Q4-2007	Q1-2008	Q2-2008
Weekly site visits		x	x	x	x	x	x	x	x	x	x	x		
QC Lab grab samples/ lab comparisons		x	x	x	x	x	x	x	x	x	x	x	x	x
Investigate remote access options				x	x									
Install remote access system					x	x	x							
Provide data for weekly report							x	x	x	x	x	x	x	x
Post data on CDEC/ store data in database												x	x	x
Certified standards.													x	x
Final report on real-time anion feasibility														x

*Q = 3 months

7. Data Quality Objectives for Measurement Data

The Dionex DX-800 is a process analyzer that has been used in process laboratories, pharmaceutical manufacturing, and industrial settings for continuous monitoring of water samples. It has not been used previously in a field setting for monitoring river water. MWQI staff have utilized the manufacturer's technical assistance during instrument installation and calibration to maximize performance of the analyzer. The overall data quality objective is to produce measurements of comparable precision and accuracy as grab samples analyzed in the laboratory. Field analyzer and laboratory anion measurements will be compared on a regular basis (Sections 10-14).

Laboratory anion analyses will be performed at Bryte Laboratory. This laboratory provides analytical, chemical, and biological services for DWR and other governmental agencies. The laboratory's "Quality Assurance Manual" is appended to this quality assurance project plan and provides detailed information on Bryte Laboratory's Quality Assurance Program including laboratory organization, sample procedures, instrument calibration and maintenance, analytical methods, quality control procedures, and reporting requirements. All activities conducted as part of this project will adhere to the protocol listed in this Quality Assurance Program (see Appendix I).

7.1 Precision and Accuracy

Precision and accuracy goals for anion measurements by the Dionex DX-800 analyzers and the grab samples analyzed at Bryte laboratory are summarized in Table 3. Accuracy will be assessed by analyzing certified standards from an outside source laboratory. Precision will be assessed by analyzing replicate samples of standards. Comparisons of field and laboratory anion measurements and determinations of precision and accuracy will continue for as long as the analyzers are in operation.

Table 3. Data quality objectives for field and laboratory anion measurements

Parameter	Method detection limit	Reporting limit	Accuracy objective	Accuracy protocol	Precision objective	Precision protocol
Field DX-800 fluoride	--not calculated	0.1*	80-120%	SRM	30%	RPD of replicates
Field DX-800 chloride	--not calculated	1.0*	80-120%	SRM	30%	RPD of replicates
Field DX-800 bromide	--not calculated	0.01*	80-120%	SRM	30%	RPD of replicates
Field DX-800 nitrate	--not calculated	0.1*	80-120%	SRM	30%	RPD of replicates
Field DX-800 sulfate	--not calculated	1.0*	80-120%	SRM	30%	RPD of replicates
Bryte Lab fluoride	0.0253	0.1	80-120%	SRM	20%	RPD of replicates
Bryte Lab chloride	0.0382	1.0	80-120%	SRM	20%	RPD of replicates
Bryte Lab bromide	0.0005	0.01	80-120%	SRM	20%	RPD of replicates
Bryte Lab nitrate	0.0109	0.1	80-120%	SRM	20%	RPD of replicates
Bryte Lab sulfate	0.0475	1.0	80-120%	SRM	20%	RPD of replicates

* not calculated – will use Bryte Lab reporting limits

7.2 Completeness

The primary purpose of this project is to test the feasibility of installing and operating real-time anion instruments at remote field stations. For the purposes of the feasibility study, the following goals have been established for data completeness: (1) data capture of at least 50% during any single month and (2) data capture of at least 75% during any yearly period. For QA/QC analyses, standards—including replicates—will be run once a month for one year starting in 2008 on the field analyzers as well as at Bryte Laboratory. The data from these standards will be used to produce control charts.

7.3 Representativeness

Grab samples of river and canal water will be collected near the middle of the channels under different hydrologic conditions to assess variations in anion concentrations and determine the representativeness of the water intakes at the RTDF stations. Hydrologic regimes that will be sampled include winter storm runoff and summer low flows. Samples will also be taken along the water intake system and analyzed to assess whether anions are lost or gained in the water delivery system (i.e., pumps, PVC pipe, and plastic tubing). Results from these investigations will be included in the final report for this feasibility study.

8. Training Requirements/Certifications

A service contract was purchased for each Dionex DX-800 analyzer and includes factory training on instrument installation and operations. All instrument operators will receive this training and have on-site access to technical documentation for the analyzers. All personnel will have a working knowledge of the *Quality Assurance Project Plan for Real-Time Monitoring of Selected Anions in the Delta* and ensure that all work is being performed according to user's manual and training guidelines. Field staff will also ensure that all documentation related to equipment maintenance and data collection is complete and accurate.

9. Documentation and Records

The Dionex analyzer produces a computer file containing each analysis, along with all calibration data and sample date and time. The calibration data include date and time, standards identification, injection amount, and calculated coefficient value. The data files will be kept on the station's computer system and transferred to a database at the MWQI Office.

On each site visit to collect grab samples, field staff will record sampling team identification, station location, sample identification number, and date and time of sample collection on a pre-printed field sheet. This form also documents the type of container and preservation methods used and any other pertinent information for the grab samples. Original field sheets will be kept at the MWQI Field Office; copies will be given to the laboratory at the time the samples are transferred there. All laboratory data will be stored in the DWR Field and Laboratory Information Management System (FLIMS) database, which is operated and maintained by the DWR Bryte Laboratory.

10. Sampling Process Design

The Dionex analyzer will perform anion analyses about every hour, 7 days a week, 365 days a year. Each analysis consists of one sample injection during which each of the 5 analytes are measured. Additionally, grab samples will be collected on a weekly basis for QA/QC requirements.

Table 4. Sampling design for analyzer QA/QC measurements

Parameter	Number of samples collected
QA/QC of field instrument 1. Anions (filtered)	Duplicate river/canal grab samples will be collected during hourly automated analyses. One will be analyzed on Field Dionex and one will be analyzed by Bryte Laboratory
Water delivery system evaluation 1. Water delivery system to analyzer 2. River/canal	One grab sample at each sampling point to be returned to laboratory for analysis to assess water system contamination

11. Sampling Methods Requirements

Surface water sampling will be limited to grab samples used for QA/QC procedures (Table 5). Anion grab samples will be collected during automated analyses and brought back to the Bryte Laboratory. Grab samples will be collected in cleaned polypropylene 1-pint bottles. No preservatives are required for these samples. The samples will be chilled to 4 degrees Celsius immediately upon collection. The containers are pre-cleaned and will be rinsed with ambient water prior to sample collection. Table 5 contains a summary of the sampling method requirements.

Table 5. Parameter table for field and laboratory anion measurements

Parameter	Number of samples	Matrix	Sample preservation	Sample container	Holding time
Field analyzers					
Dionex DX-800	1 sample hourly, seven days per week	Surface water	None	N/A	N/A
Lab Grab Samples					
Dionex DX-500	1 River sample and 1 delivery system sample once a week	Surface water	None	1-pint polypropylene bottle	28 days

12. Sample Handling and Custody Requirements

All samples will be collected and handled in a manner consistent with protocol established in the MWQI Field Manual except where changes are required by this project. All anion grab samples will be received by the DWR Bryte Laboratory (in West Sacramento) following standard chain of custody procedures (Appendix 1). The collection bottles will be marked by MWQI field staff with a code number relating to the analysis requested. The laboratory will follow established protocols for analyzing these samples (see Appendix 1).

13. Analytical Methods Requirements

EPA method 200.8 is used to analyze anions at the field stations and at Bryte Laboratory. At the field stations, analyses will be done on the Dionex DX-800 Process Analytical Ion Chromatograph units. In the analyzer, a continuous flow of sample water is provided by the pump

and delivery system. Every hour a sample is injected and concentrated on a column. Certain analytes are retained on the column longer than others. After the sample comes off the column, it goes through a suppressor, which lowers the background noise. The sample then flows to the conductivity detector where the analytes are detected. The result on the computer screen is a chromatograph with each analyte having its own retention time and integrated peak that determines its concentration. The Bryte Laboratory uses a Dionex DX-500, which employs a similar process in sample preparation and analyte detection.

14. Quality Control Requirements

Precision and accuracy of anion (samples) analyses will be assessed at both field stations and at Bryte Laboratory. Field analyzer precision will be determined using triplicate measurements of certified standards. All grab samples for laboratory anion analysis will be done in duplicate to assess the precision of the laboratory analyzer. Accuracy of both field and laboratory measurements will be assessed using standard reference materials. Precision and accuracy determinations will be done on a monthly basis at the field stations and during each analytical run at Bryte Laboratory. If QC samples fall out of desired control limits (see Table 4), the data will be flagged in the database.

To check whether anions are lost or gained in the water supply system, a comparison will be conducted of anion levels in grab samples collected both near the water supply intake and in the aqueduct or river. To ensure the comparability of field and laboratory anion measurements, grab samples from each Dionex flow-through system will be collected biweekly and analyzed by the field instruments and at Bryte Laboratory.

15. Instrument/Equipment Testing, Inspection, and Maintenance Requirements

The Dionex DX-800 analyzer will be thoroughly inspected on each routine site inspection and calibrated as needed. Standards and deionized water will be replaced monthly; replacement intervals for other consumable components are listed in Appendix 2. In addition to information gathered on site visits, remote access to analyzer systems will be possible via computerized network connection giving real-time access to a wide array of information including system errors. Errors and other unknown problems will trigger a visit to the site for evaluation and correction of the problem.

The laboratory Dionex analyzer is tested, inspected, and maintained by the Bryte Laboratory following guidelines found in their Quality Assurance Manual (see Appendix 1).

16. Instrument Calibration and Frequency

The Dionex DX-800 analyzer will be manually calibrated as needed using a 5-point calibration. The stock standard is a mix of the 5 anions of interest. The stock contains 10,000 mg/L of chloride and sulfate, 1000 mg/L of nitrate, 100 mg/L of fluoride, and 50 mg/L of bromide; it will be prepared by the MWQI staff using NIST-Traceable Standard Reference Materials. Calibration results will be recorded on the analyzers computer; backup copies will be kept on computers at MWQI headquarters. Calibration results will be placed as metadata in the database. In addition, calibration can be remotely initiated at anytime using remote desktop program. The laboratory anion analyzer is calibrated by Bryte Laboratory using NIST-Traceable Standard Reference Materials following guidelines found in its Quality Assurance Manual (see Appendix 1).

17. Inspection/Acceptance Requirements for Supplies

All consumable supplies (potassium hydroxide, analytical columns, etc.) will be purchased from Dionex Corp. and will have undergone rigorous inspection at the factory. The deionized water and standards used for calibration of the field instrument will be prepared by MWQI staff and analyzed at Bryte Laboratory to ensure their quality.

18. Data Acquisition Requirements

All data used for this project will be obtained through MWQI monitoring activities, and no outside data sources will be required.

19. Data Management

19.1 Grab Sample Data

Before grab samples are collected, a sampling request is entered into the FLIMS database maintained by Bryte Laboratory. All pertinent information about the samples to be collected (site, date, type of analyses requested, required sampling container, sampling protocol, etc.) are required. FLIMS generates all of the field forms and bottle labels including unique sample code numbers. These forms along with the labeled bottles are taken into the field. Samples are collected using established protocols. The grab samples are then returned to Bryte Laboratory where they are submitted to the laboratory auditor, who verifies the chain of custody and records in the database any changes in sampling information. Once the samples enter Bryte Laboratory, they are tracked through all analytical procedures; this information is recorded in the FLIMS database.

19.2 Telemetered Data

Roughly every 50 minutes, data from the field instruments are sent via FTP connection to a server that resides in the DWR computer network. This server is then polled from an internal production server at 25-minute intervals to obtain, compile, and import data into a database for further analysis. This entire process is completed using automated scripting techniques and scheduled tasks set up on a number of personal computers and servers. Once inside the database, the data are filtered and made available on the CDEC Web site as well as in the RTDF project weekly report.

20. Assessment and Response Actions

Field and laboratory analyses, QA/QC results, calibration parameters, and field notes will be reviewed on a weekly basis by the project managers (Pimental and Gonzalez) and the quality assurance manager (Ngatia) to ensure that all data quality objectives are being met (Section 7 and Table 4). Certified standards will be analyzed once a month to ensure data quality. If problems are detected, the project managers will consult with field staff and instrument manufacturers to rectify the situation. Corrective actions could include more frequent site service, more frequent instrument calibration, or other actions as deemed necessary.

21. Reports

A final report on the feasibility of real-time anion monitoring will be prepared by June 2008. The final report will summarize all QA/QC data collected during station setup and operation. This report will be prepared by the project managers (Pimental and Gonzalez) with assistance from

the quality control manager (Ngatia). Copies will be sent to the individuals on the distribution list at the start of this report.

22. Data Review, Validation, and Verification Requirements

Field and laboratory anion analyses, QA/QC results, calibration parameters, and field notes will be obtained from the RTDF project Access database and reviewed on a weekly basis by the project managers (Pimental and Gonzalez) and the quality assurance manager (Ngatia) to ensure that all data quality objectives are being met (Section 7 and Table 4). Decisions to reject or qualify data will be made by the project managers.

23. Validation and Verification Methods

All QA/QC, real-time, and laboratory anion data and calibration results will be reviewed by the project managers (Pimental and Gonzalez) and the quality assurance manager (Ngatia). Any real-time or laboratory anion measurements that fall outside of the QA/QC ranges identified in Table 4 and Section 7 will be flagged in the database. Obvious outliers and erroneous data due to incorrect integration or retention times will be removed from the CDEC Web site and will be flagged in the database. If recording errors are detected, the problem will be isolated and corrected, and the values from the printout will be included in the finalized data. However, only the computer output data will go into the finalized MWQI data sets if no errors are detected; this protocol will minimize the potential for typographical errors in final data products and reports. All problems with interim and final data products will be noted in the database and final report.

24. Reconciliation with Data Quality Objectives

Several times per month all QA/QC parameters will be computed (field and laboratory precision and laboratory comparison results) and corrective actions taken if necessary. If data quality indicators do not meet criteria stated in Section 7 and Table 4, then values will be flagged in the database or discarded. The cause of failure will be evaluated, and corrective measures will be implemented. If the cause is instrument failure, site visits and instrument calibration intervals will be reassessed and improved. If problems are caused by field or laboratory personnel, team members will be retrained. Detailed assessments of all data quality problems will be discussed in the final report.

Appendix 1

Bryte Chemical Laboratory Quality Assurance Manual

Appendix 2

Dionex DX-800 Replacement intervals for consumable parts

Part	Replacement schedule	Cost
AS19 Analytical Column	6 mo – 1 yr	$850
AS19 Guard Column	6 mo – 1 yr	$275
EluGen II KOH Cartridge	Approx. 1 yr	$985
ASRS ULTRA II (2mm) Anion self regenerating suppressor	Approx. 1-2 yrs	$950
CR-ATC Continuously Regenerated Anion Trap Column	No strict replacement schedule.	$950

Appendix 1

Bryte Chemical Laboratory Quality Assurance Manual

May 2006

State of California The Resources Agency Department of Water Resources

Bryte Chemical Laboratory
Quality Assurance Manual

May 2006

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1. Introduction

The Bryte Chemical Laboratory's primary role within the Department of Water Resources is to provide analytical, chemical, and biological laboratory services for DWR. As a secondary role, the laboratory provides these same services to other governmental agencies. This manual addresses the quality assurance and quality control measures used by the laboratory in determining the organic, inorganic, and biological entities found in California waters.

This QA manual addresses all activities that are essential in the operation of the analytical laboratory. The principles presented in this manual are used to ensure the laboratory is providing information that is factual, precise, accurate, reliable, and adequate for its intended use.

This manual is designed to meet the U.S. Environmental Protections Agency policy guidelines as outlined in the *Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans*, QAMS-005/80, and also to meet the California Department of Health Services, Environmental Laboratory Accreditation Program.

2. Definition, Purpose, and Scope

Definition of Terms

Quality Assurance Program: An orderly assemblage of management policies, objectives, principles, and general procedures by which an agency or laboratory outlines how it intends to produce data of known and accepted quality.

Quality Assurance: The total integrated program for assuring the reliability of monitoring and measurement data. QA is a system for integrating the quality planning, quality assessment, and quality improvement efforts to meet user requirements.

Quality Control: The routine application of procedures for obtaining prescribed standards of performance in the monitoring and measurement process.

Quality Assessment: The overall system of activities to provide assurance that the QC task is being performed effectively. Quality Assessment involves a continuing evaluation of performance of the production system and the results produced.

Standard Operating Procedure: A detailed written procedure designed to systematize and standardize the performance of the procedure.

Purpose of Manual

The purpose of this manual is to describe the QA/QC program for all laboratory practices in order to generate the most precise and accurate data possible. To achieve this purpose, a comprehensive and scientifically sound QA plan has been implemented and is now used.

Scope - Objectives

The ultimate goal of the laboratory is to produce quality data that is accurate, precise, complete, representative, and compatible. While proper validated methodologies are necessary, these alone are not sufficient to assure data quality. The QA plan is designed to control and monitor laboratory activities, ensuring the laboratory meets the data quality objectives listed above.

The QA program will be carried out under the direction of the Laboratory QA Officer who reports directly to the Chief of the Bryte Chemical Laboratory. It covers all aspects of sample receiving, storage, preparation, analysis, and reporting.

Standard QC procedures, data reduction, and reporting will be in compliance with requirements in *Standard Methods for Examination of Water and Wastewater*, 19th ed. or later editions. Written SOPs for sample receipt, chain of custody, preservation, storage, preparation, analysis, safety, and reporting shall be followed. Log books, printed documents, data, or other written documentation shall be available to describe the work performed in each of the following stages of analysis:

- Chain of custody
- Sample preservation
- Sample receipt
- Sample storage
- Sample preparation
- Sample Analysis
- Data reduction
- Data reporting
- QA/QC

3. Organization and Responsibility

Executing an effective QA program in the laboratory demands the commitment and attention of both management and staff. All laboratory personnel within the organization play a vital role in assuring a continued commitment to the quality of work accomplished. (See Figure 1, Bryte Chemical Laboratory Organizational Chart). The laboratory staff is highly qualified and trained in the following areas:

- Gas chromatography/mass spectrometry (GC/MS)
- Gas chromatography (GC)
- High performance liquid chromatography (HPLC)
- Purge and trap techniques
- Ion chromatography (IC)
- Flame atomic absorption spectroscopy (AA)
- Graphite furnace atomic absorption spectroscopy
- Colorimetric analytical techniques
- Carbon analysis (TOC, DC)
- Wet chemical analysis
- Analytical method development
- Emission spectroscopy (ICP, ICP/MS)
- Sample preparation
- Fecal coliform
- Chlorophyll and pheophytin
- Phytoplankton

Chief of the Bryte Chemical Laboratory

The Chief of the Bryte Chemical Laboratory is responsible for all operational activities within the laboratory and is accountable for all data generated by the laboratory. QA responsibilities consist of:

- Final review of all data generated by the laboratory
- Final authority to release data to requestor
- Final authority on all analytical procedures and SOPs used by laboratory personnel
- Coordinates with the Laboratory QA Officer in implementing the laboratory QA plan and its policies, revisions, and any corrective action to ensure compliance
- Periodic audits of the QA plan to ensure the objectives and procedures are being followed

Laboratory QA Officer

The Laboratory QA Officer is independent and reports only to the Chief of the Bryte Chemical Laboratory. The Laboratory QA Officer:

- Recommends QA policy to the Chief of the Bryte Chemical Laboratory
- Develops and manages the laboratory QA plan, revises it as needed
- Oversees QC practices in the laboratory and data management
- Helps develop analytical procedures
- Develops precision and accuracy guidelines/criteria
- Reviews data quality and laboratory performance audits
- Conducts data quality and laboratory performance audits
- Prescribes and monitors corrective actions
- Recommends QC training for personnel
- Coordinates all QC/QA activities
- Approves SOPs
- Monitors laboratory performance, turnaround, and holding times

Data Control Section

The Data Control Section is responsible for all data coordination and review. Staff performs the following:

- Reviews all analysis report forms for completeness
- Reviews all analysis request forms to ensure compliance within contractual obligations
- Ensures requestor receives the final completed data report
- Maintains records and archives of all data reports

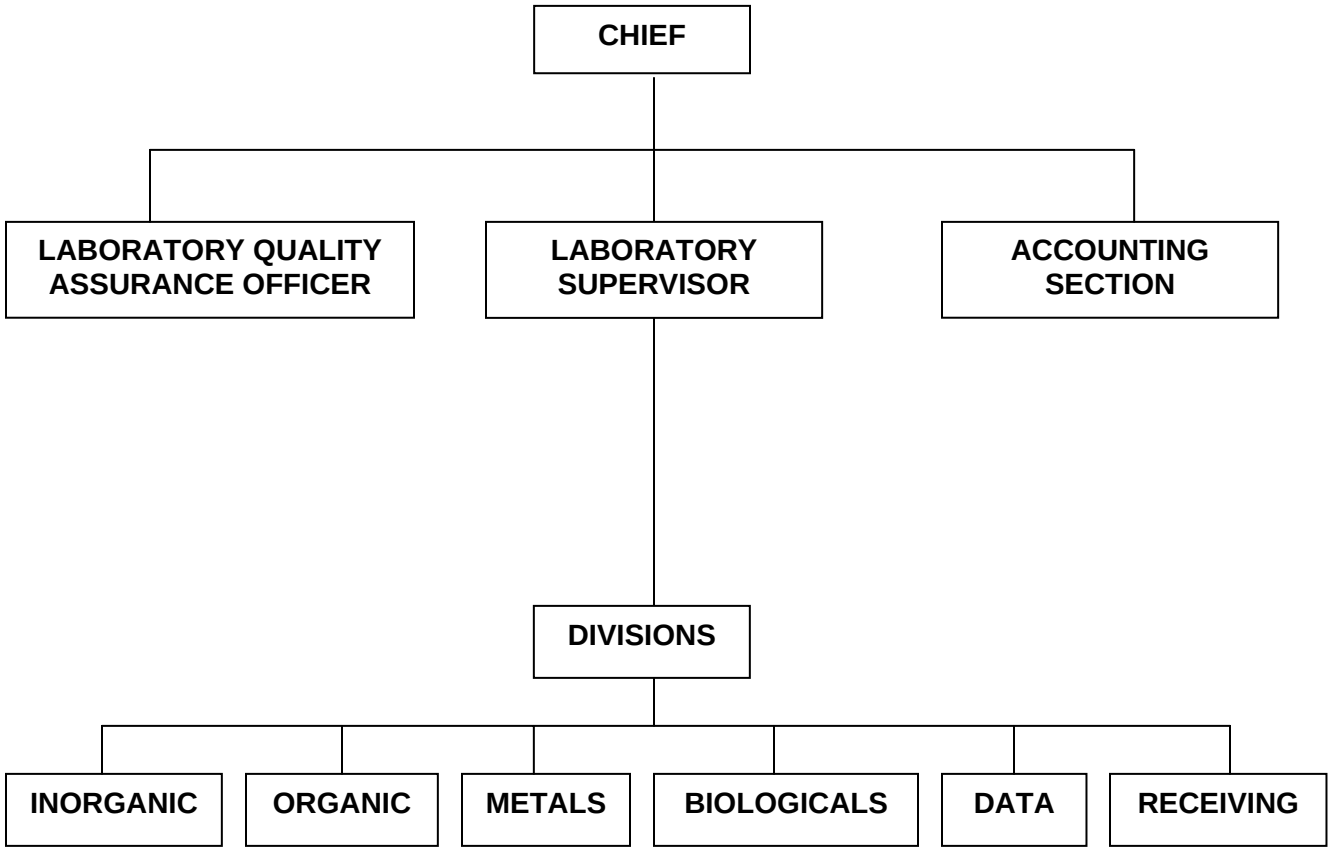
Laboratory Staff

Since the greatest amount of responsibility for a successful QA program rests with the analysts, it is important that they be highly qualified and competent. New and experienced laboratory personnel shall be carefully trained for new specific work assignments. Laboratory personnel have on-site access to technical journals and textbooks as well as access to the Resources Agency Library services. Combined administrative and technical staff meetings will be held to help provide a good

information exchange forum. Laboratory personnel are responsible for:

- Having a working knowledge of the QA plan
- Ensuring that all work generated is in compliance with QC acceptance criteria
- Performing all work according to written SOPs
- Ensuring that all documentation to their work is complete and accurate
- Ensuring that acceptance of any data outside QC criteria must be approved by laboratory management
- Maintaining records for a all QC data
- Notifying management immediately of any QC issues
- Writing and updating SOPs
- Meeting holding and turnaround times

Figure 1. Bryte Chemical Laboratory Organizational Chart



4. Sample Procedures

The laboratory does not take part in any of the actual sampling activities, but the sample collection process is a major concern of the laboratory. Since the ultimate quality of data generated begins with the sample collection process, the laboratory can assist in the sampling procedure by providing consultation and assistance to project managers and any contractors involved in a project. (See DWR Sampling Manual.)

Sample Containers and Holding Times

The laboratory supplies all necessary sampling materials to DWR field sampling units. Using properly cleaned containers and correct preservatives as well as adhering to proper holding times are essential factors for maintaining sample integrity and representativeness. Requirements for sample containers, preservation techniques, and holding times are found in one of the following references (or later editions):

- *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, et al., 19th Edition, or later
- *Federal Register* Volume 49, No. 209, Friday, October 26, 1984, EPA, 40 Code of Federal Regulations, Part 136
- *Handbook for Sampling and Sample Preservation of Water and Wastewater*, EPA 600/4-82-029, September 1982 (Does not apply to drinking water)

SOPs for cleaning and preparing glassware and sample containers are strictly complied with to ensure that the sample is not contaminated during the collection process due to containers.

Appropriate volumes of the sample must also be collected to ensure that the required detection limits can be met, the QC samples analyzed, and any necessary sample reanalysis performed.

For proper containers, holding times, preservation techniques, and volumes required, see Appendix A (Water Sample Collection Information).

Sample Submittal

Samples are brought to the laboratory by delivery services or field sampling crews. Any sample taken in a nonstandard container, improperly preserved, or shipped in an unacceptable manner may be rejected. Each sample or group of samples needs to be entered into the Field and Laboratory Information Management System (FLIMS). This can be done either manually in the laboratory or in the field and then electronically transferred directly into FLIMS. All pertinent field data is tracked by FLIMS such as the date, time, location, field sampler, field data, laboratory tests requested, etc. When the samples are completely logged in, FLIMS notifies the laboratory personnel that samples need to be analyzed.

Sample Storage and Handling

The samples received by the laboratory are placed in appropriate storage or sent directly to the test area. The storage areas are located in the receiving room and consist of refrigerators at 4°C, freezers at -10°C, and designated storage cabinets for sample types (i.e., metals, standard minerals, etc.). Once the analysis is completed, the remaining sample is kept for 30-60 days in storage, and then discarded. If a contracting officer should request return of a sample prior to the expiration interval, it will be returned in a manner that meets the required criteria.

Quality Assurance Sample

To evaluate and ensure acceptable results, the laboratory requires that samplers submit travel blanks, field blanks, and/or duplicate samples with their samples. For specific requirements, see DWR Water Quality Sampling Procedures.

5. Sample Custody Procedures

A Chain of Custody form must be completed for samples received by the laboratory which may be used as evidence for enforcement purposes. Once a sample is received, the Chain of Custody Officer or the alternate is notified. All information is then transcribed to the Chain of Custody form and the sampler signs the form, witnessed by the Chain of Custody Officer or alternate. The sample is then transferred to the appropriate location to wait for analysis. For each transfer of physical custody, an entry of disposition and one of receipt is made on the custody form.

While in the laboratory, samples are stored in a secure area under appropriate preservation and environmental conditions. Following the completion of the analysis, the samples are stored until the results are submitted to the Program Manager and permission to discard has been received. A notation of completion is made on the Chain of Custody form, and the document is then filed with the analysis report. Copies of the files are maintained in the DWR archives.

6. Calibration and Measurement Procedures

Calibration of instruments is required to ensure that the analytical system is operating correctly and functioning at the proper sensitivity to meet established detection limits. In general, calibration is accomplished by measuring instrument response to standards containing the analytes in known concentrations while being in compliance with manufacturer's recommendations.

Instrument Calibration and Frequency

Today's complex instrumentation and calibration frequencies are extremely varied; therefore, a bound notebook is assigned to each instrument to log the following:

- All maintenance performed
- All daily sensitivity checks and/or calibration results where applicable according to methodology found in SOP
- All manufacturer's maintenance and repairs

Each log entry will contain the date, operator's name, and operation performed (i.e., maintenance, sensitivity check, etc.).

Calibration is accomplished on a daily basis or whenever the following instruments are used:

- Atomic Absorption (flame and furnace)
- Spectrophotometers
- Gas-Liquid Chromatographs
- Ion Chromatographs
- Mass Spectrometers
- Auto Titrators
- Auto Analyzers
- Atomic Emission (ICP and ICP/MS)

Other instruments may require weekly, monthly, quarterly, or even semiannual calibration (i.e., balances, ovens, exhaust hoods, etc.). Once a standard calibration range has been established, at least three standards are normally used in daily standardization where applicable. For specifics, see the SOP for a particular analytical procedure. If a problem arises which cannot be corrected by the instrument operator, then the Laboratory QA Officer is notified. The officer will coordinate the necessary diagnostic and corrective measures to be implemented. Documentation will be provided a in the instrument log book.

Calibration Standards/Reagents Preparation

A critical area in the generation of quality data is the quality, purity, and traceability of the standards and reagents used in analytical calibration procedures. All primary reference standards and standard solutions used by the laboratory are obtained from the National Institute of Standards and Technology or commercial manufacturers. All standards, standard solutions, and reagents are validated prior to being used. Validation procedures range from a check for chromatographic purity to verification of concentration of the standard using standards prepared at a difference time or from a different source.

All Stock Standards are labeled as to the following:

- Name and concentration of stock
- Method of preparation
- Date prepared/Preparer's name
- Supplier, purity, lot number, and expiration date
- Any other pertinent information

New working standards are compared to the remainder of the current working standards for any concentration differences, formation of precipitates, and any signs of deterioration. Reagents are also examined for purity by subjecting an aliquot to the analytical method for its intended use. For example, reagent water, organic solvents, or acids are analyzed for possible contamination prior to use.

7. Analytical Procedures

Analytical methods are derived from the latest editions of one of the following references:

- *Methods for Chemical Analyses of Water and Wastes*, EPA-600/4-79-020 (revised March 1983) (Not used for drinking water.)
- *Standard Methods for the Examination of Water and Wastewater*, 19th Edition or later, APHA, American Water Works Association, Water Pollution Control Federation, Washington, D.C. (1992)
- *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, Techniques of Water Resources Investigations*, USGS, Book 5, Washington, D.C. (1985)
- *Annual Book of American Society for Testing and Material Standards*, Volumes 11.01 and 11.02, ASTM, Philadelphia, Pennsylvania (1988)
- *Official Methods of Analysis*, 14th Edition, AOAC International, Arlington, Virginia (1984)
- *Methods for Organic Chemical Analysis and Municipal and Industrial Wastes*, EPA 600/4-82-057, (1982)
- *Guidelines Establishing Test Procedures for the Analysis of Pollutants Under Clean Water Act*, Federal Register, EPA, 40 CFR, Part 136, (1984)
- *Biological Field and Laboratory Methods*, EPA-670/4-73-001, (1973)
- *Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods*, EPA, SW846, Volumes 1A, 1B, 1C, and II, (1986)

For a specific analytical method used, see Appendix F.

Standard Operating Procedure

Analytical methods chosen are dependent upon certain objectives, some of which consist of precision and accuracy, type of sample matrix, and quantitative sensitivity. Each analytical method routinely used is documented in the form of a SOP which contains complete detailed instructions to standardize the expected performance of the analytical method. Contents of a laboratory SOP are given in Appendix B. Any deviations from published methodology are documented in the SOP.

Analytical Methodology Verification

Before any analytical method is routinely used to generate data, the method is validated. Criteria used to validate a method consist of the following:

- Method selection by senior staff
- Testing of method verifying reporting limits, dynamic range, matrix effects, precision, and accuracy criteria
- Data acceptance criteria must be approved by the Laboratory QA Officer and Chief of the Bryte Chemical Laboratory
- Final documentation of the method in a written SOP

8. Data Reduction, Validation, and Reporting

The final step in analyzing samples is to review the data collected prior to reporting. The analytical data generated within the laboratory are extensively checked and cross-checked for their accuracy, precision, and completeness. The validation process consists of data generation, reduction review, and finally reporting results to the submitter.

The primary responsibility for the generation of accurate data rests with the analyst. The analyst performs the data calculation functions and is responsible for the initial examination of the finished data. All data reduction steps applied to the raw data is outlined in the appropriate analytical SOPs. Each analyst reviews the quality of their work based on the following guidelines:

- The appropriate SOP has been followed
- Sample preparation is correct and complete
- Analytical results are correct an complete
- Blank correction procedures and followed, if applicable
- QC samples are within established QC limits
- All documentation is complete, including analysis report, QC form and QC charts

The QC procedures outlined in the analytical SOP are used for the preliminary validation of the results along with any historical data, if available. When applicable, correlation checks are used to validate the data, such as anion-cation balances, specific conductance versus dissolved solids, dissolved solids versus calculated dissolved solids, Biological Oxygen Demand versus suspended solids, Chemical Oxygen Demand or Total Organic Carbon, etc. After data reduction and validation steps are computed, the analyst enters the data into the FLIMS and releases the QC batch.

The data package is the forwarded electronically in the FLIMS to the QA Officer who evaluates the data along with all pertinent QC results such as laboratory control standards, matrix spikes, surrogates, duplicates, blind duplicates, blind Performance Evaluation samples, and labortory performance records, as well as historical records to help form a basis for acceptance of data. If the data package passes QA/QC criteria, it is released in the FLIMS to the senior staff.

A data package containing the required QC batches for each sample submittal is then reviewed by senior staff for final validation, completeness, and acceptance. The final review is based on the following criteria:

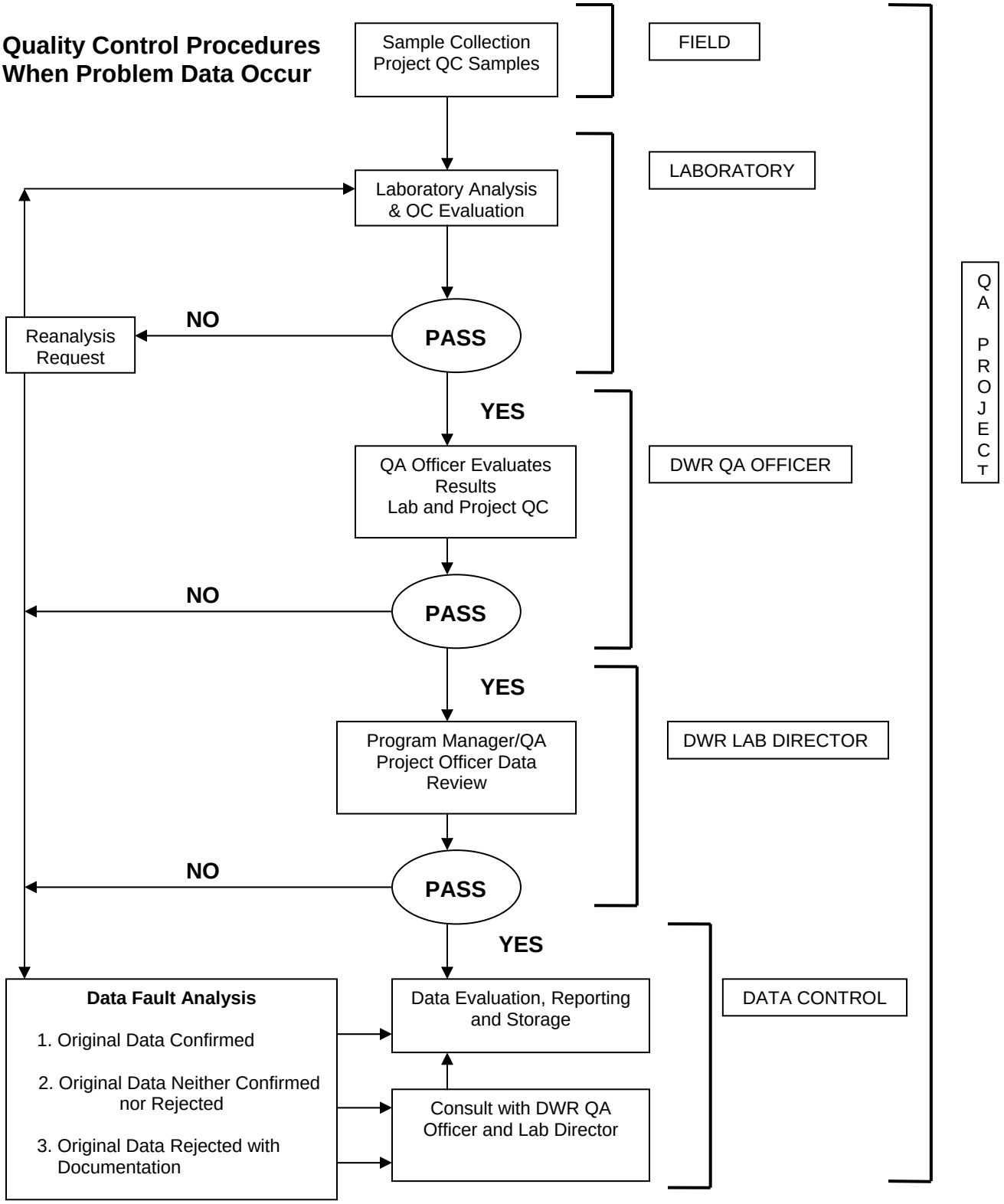
- Calibration data reviewed
- Appropriate methodologies used
- QC samples within established guidelines
- Comparison of historical data when available
- Correlation checks reviewed (i.e., anion-cation balance, electrical conductivity versus total dissolved solids, etc.,) when applicable.
- Evaluation of data in general by comparability, assessment, and reasonableness of sample types, (i.e., wastewaters, surface waters, groundwaters, etc.)
- Ensures completion of all analytical work requested

After validation and review by senior staff, the approved data package is incorporated into a final analysis report. The final report is released to the submitter either in a printed format with all the appropriate information or sent to the submitter by FLIMS in electronic format. The full data package is then archived for possible future use.

Errors or problems which may occur are documented and transmitted to the appropriate section. The cause of the errors is then addressed either by further training or reevaluation of the analytical method SOPs to ensure quality data is generated at the analyst level.

See Figure 2. Data Validation Flowchart on the following page.

Figure 2. Data Validation Flowchart



9. Internal Quality Control Checks

Internal QC is the routine activities and checks such as calibrations, duplicate analysis, spiked samples, etc. included in normal procedures to control accuracy and precision of the measurement process. It determines whether the laboratory operations are within acceptable QC guidelines during sample analysis.

Blanks

Field Blanks are check samples which monitor contamination originating from the collection, transport, and storage of environmental samples. Laboratory prepared blank water is supplied to field personnel for processing in the same manner as samples; this includes field filtration and addition of preservatives.

Travel Blanks are prepared in the laboratory from ultra-pure water. They are supplied to field personnel with each batch of empty sample bottles and are returned with the collected samples. Travel blanks are routinely used for volatile organic samples to determine whether sample transport has contaminated the samples collected.

Method Blanks are prepared from laboratory blank water, substituted for samples, and analyzed with every sample set. Method blanks are used to determine the level of contamination that exists in the analytical procedure. Contamination may or may not lead to elevated concentration levels or false positive data. Ideally, the concentration of an analyte in the method blank is below the method detection level for the analyte. However, for some analytical methods, elimination of blank contamination is extremely difficult; therefore, each analytical SOP has a method blank level of acceptance. If the acceptance contamination level is exceeded, the sample set is reanalyzed.

Calibration Standards

Calibration standards are routinely run with every sample set. Calibration standards must fall within established QC limits before any sample results can be accepted. The limits are found in the particular analytical method SOP being used. If the calibration standards are unacceptable, the sample results are rejected, corrective action taken, and the samples reanalyzed.

Check Standards

The check standard is usually a midrange calibration standard used to monitor the analytical method. The check standard is analyzed every ten samples to provide evidence that the laboratory is performing the method within accepted QC guidelines. As long as check standard results fall within established control limits, the analysis can continue. If check standard results fall outside the control limits, the data are suspect and the procedure is stopped. The analytical procedure is checked for error step by step by the analyst. Once the procedure is again acceptable, reanalysis of samples begins with the last check standard that was within acceptable control limits.

Laboratory Control Sample

When one is available, the LCS is analyzed routinely to verify the analytical method is in control and to also serve as a second source verification for the calibration standards of all routine analyses. The concentration of the LCS is within the working range of the analytical method and does not require extensive pretreatment, dilution, or concentration prior to analysis. The sources include, but are not limited to: QC samples, EPA, commercially prepared samples, or samples prepared in-house with different sources than those used in the calibration standards. Recovery data from the LCS are compared to the control limits which are established for those analytes monitored by the LCS. Before any data can be accepted, the analytes of interest in the LCS must fall within their expected control limits. If, for any reason, the results fall outside those limits, the sample results in the associated batch are unacceptable. Corrective steps are taken and filed with the QA/QC Officer. After the corrective action has been proven effective and the LCS is within the specified control limits, the samples are the reanalyzed.

Internal Standards

An internal standard is used in the more difficult analyses such as ICP, ICPMS, GC and GCMS. The internal standard is similar in analytical behavior to the analytes of interest and is added to all samples, standards, and blanks. Usually, more than one internal standard is added to each sample to evaluate the measurement of the sample throughout the entire time of analysis. The internal standards help determine the individual response factors used to calculate the concentrations of the analytes of interest.

$$RF = (A_s)(C_{is})/A_{is})(C_s)$$

where:

A_s = Area for reference analyte to be measured

A_{is} = Area for the internal standard

C_{is} = Concentration of the internal standard (µg/L)

C_s = Concentration of the reference analyte to be measured (µg/L)

The concentration of the analyte is calculated by:

$$C_a = (A_a/A_{is})(C_{is}/RF)$$

where:

C_a = Concentration of the analyte in sample (µg/L)
A_a = peak area of the analyte
RF = Response factor

The monitoring of the internal standards area counts is also used as a continuing check on instrument system performance. An average area count is established for each internal standard and any analytical run in which the internal standard area count falls outside the established criteria, the run is aborted, the cause is corrected, and the sample is reanalyzed.

Surrogate Compounds

Surrogate compounds are used in the analysis of organic compounds by gas chromatography (GC) and/or by a combination of gas chromatography and mass spectrometry (GC/MS). Like the internal standard, the surrogate compounds are similar in analytical behavior to the compounds of interest and are added to all samples, standards, and blanks. A known amount of surrogate is added to monitor the analytical performance of the method. The results of the surrogate compounds must fall within the established QC criteria for the analytical method. Samples that are outside the QC limits are reprepped and analyzed. If the reanalysis confirms the original analysis, both sets of data are reported with a flag attributing the out of control data to matrix interference.

Samples Duplicates

Duplicates are environmental samples divided into two separate aliquots analyzed independently to determine the repeatability or precision of the analytical method. The difference in the duplicate results must be within established control limits to ensure the generated data meet the quality assurance objectives for the particular analytical method.

Matrix Spike/Matrix Spike Duplicates

A spiked environmental sample is used to check for any matrix effects on the precision and accuracy of an analytical measurement. One out of every 20 samples or one per batch is spiked twice with a known concentration of the analyte of interest, and then analyzed in a normal manner. The percent recovery and relative percent difference are calculated and the results must fall within established control limits to ensure the generated data meets the QA objectives for the particular analytical method used.

Performance Evaluation Samples

PE samples are routinely issued to the analyst to monitor both the analyst's work and analytical procedure. The recorded results are reviewed by both the Laboratory QA Officer and senior staff. If any problems occur, follow-up corrective action is taken. PE samples may be in the form of blanks, previously analyzed environmental samples, split samples, or standard reference materials such as EPA, USGS, etc.

Standard Method of Additions

Standard method of additions is the practice of adding known concentrations of analyte to a sample so that matrix effects (interferences) are minimized. Whenever sample interference is suspected, the method of standard additions is employed to verify the quality of the data.

Bracketing

Bracketing is the use of standards to bracket the apparent concentration of the analyte in the sample. The sample is bracketed between a high and low standard, the standards being as close to the measured sample value as possible, usually ±10 percent. The calculated results are then done by interpolation as follows:

$$C_s = [((R_s - R_{ls})(C_{hs} - C_{ls})/(R_{hs} - R_{ls})) + C_{ls}](\text{dilution})$$

where:

C_s = Sample concentration
R_s = Response of sample
R_{hs} = Response of High Standard
R_{ls} = Response of Low Standard
C_{hs} = Concentration of High Standard
C_{ls} = Concentration of Low Standard

Normally, bracketing is used where precision of the methodology is poor. By bracketing, verification of the data quality can be obtained.

10. Performance and System Audits

Performance and system audits are an essential part of QA to ensure that the laboratory is statistically generating consistent valid data. A system audit consists of reviewing laboratory conditions, practices, equipment, staff, and procedures used to generate quality data. Performance audits verify the ability of the laboratory to correctly identify and quantitate compounds in blind check samples. The laboratory currently participates in several ongoing auditing programs on a regular basis. The audits can be categorized into external and internal audits.

External Audits
The laboratory participates in the following external audit programs:

- Water Pollution/Supply Performance Evaluation Studies, U.S. Environmental Protection Agency
- Standard Reference Water Sample Project, U.S. Geological Survey
- San Joaquin Valley Drainage Program interlaboratory comparison studies
- Split sample analysis with other laboratories both public and private

Internal Audits
Regular audits using an in-house blind reference sample are conducted for specific routine procedures. The results of the analyses are evaluated by the Laboratory QA Officer and the Chief of the Bryte Chemical Laboratory. System audits are conducted to assess the QA implementation in the laboratory. Inspection of QC charts, analytical procedures, equipment logs, and QA documentation in general is evaluated and reviewed for compliance and any needed operational changes.

In addition, informal audits are conducted by the Laboratory QA Officer as required when accuracy and precision of analyses appear to be drifting out of control. These audits may include the use of QC samples, varied matrices, calibration of instruments, and observation of the analyst to identify additional training of clarification needs, and may require changes in the analytical SOP.

The control limits are determined by calculating the mean (X) of a minimum of 20 data points and the standard deviation (S_d) to generate a control chart that has a center line X and an upper and lower line S_d. Control charts are used to monitor trends in the data which could result in corrective actions.

$$X = \frac{\sum D}{n}$$

D = data points
n = number of data points

$$S_d = \sqrt{\frac{n\left(\sum x^2\right) - \left(\sum x\right)^2}{n(n-1)}}$$

Upper Control Limit (UCL) = $x + 3S_d$
Lower Control Limit (LCL) = $x - 3S_d$
Upper Warning Limit (UWL) = $x + 1.5S_d$
Lower Warning Limit (LWL) = $x + 1.5S_d$

11. Preventative Maintenance

Preventative maintenance is routinely performed on all analytical equipment and instruments to minimize the amount of downtime and to maintain data quality. Equipment manuals, troubleshooting guides, and log books are available for maintenance support. Critical spare parts are kept on hand for laboratory instrumentation that is routinely repaired by laboratory staff. The inventory is monitored and maintained to avoid extended periods of downtime.

Service Contracts

The laboratory maintains service contracts with manufacturers and specialty companies for complex analytical equipment (i.e., GC and ICP/MS).

General Maintenance

Chemists are responsible for the routine daily maintenance of their instruments per the manufacturer's recommendations and for documenting repairs in the equipment maintenance log books. Designated laboratory personnel are trained and responsible for more complex maintenance procedures. All necessary repairs are performed by trained staff or factory service engineers. The Chief of the Bryte Chemical Laboratory will be informed of the need for, and the performance of all major maintenance activities that may directly impact sample analysis schedules.

Equipment Log Books

Equipment log books are maintained for all analytical instruments and equipment used in the laboratory. Each entry in the log book includes the date, the nature of the entry, and the name of the individual responsible for the entry. The following information is recorded in the log books:

- Results of all sensitivity checks (verifying the equipment is operating according to QA criteria for the method and/or meets the manufacturer's specifications)
- All scheduled maintenance performed
- Any major or minor problem encountered, a brief description, corrective action required, and a list of any parts replaced
- Verification of equipment operation after any maintenance is performed by designated laboratory staff

The equipment log books are periodically reviewed by the Laboratory QA Officer for compliance and problem areas in the equipment.

12. Routine Procedures Used to Assess Data Quality

The effectiveness of data quality assessment in a QA program is measured by the quality of the data generated by the laboratory. Data quality is evaluated in terms of precision, accuracy, comparability, and completeness.

Precision and Accuracy

Precision is the degree to which the measurement is reproducible among replicate observations, and accuracy is a determination of how close the measurement is to the true value. Laboratory precision and accuracy have been established for all analytical procedures used and are assessed for each sample set that is analyzed. The precision of analytical data is determined routinely by running duplicate tests in samples, laboratory control standards, and matrix spikes within the sample set. Accuracy is evaluated by analysis of spiked samples. Sample spikes are prepared by addition of a known amount standard solution to a sample. The spiked sample and unspiked sample are then analyzed for the parameter of interest. Precision and accuracy assessment utilize control charts and well established statistical procedures found in the following reference publications:

- *Handbook for Analytical Quality Control in Water and Wastewater Laboratories* (EPA 600/4-79-019, March 1979)
- *Quality Assurance Practices for the Chemical and Biological Analyses of Water and Fluvial Sediments, Techniques of Water Resources Investigations,* USGS, Book 5, Chapter A6, 1982
- *Manual of Analytical Quality Control for Pesticides and Related Compounds in Human and Environmental Samples* (EPA-600/1-79-008, January 1979)

Comparability

Comparability expresses the confidence with which the data set can be compared to other data sets measuring the same properties. See Section 8.1, Data Validation and Reporting, for procedures used to evaluate comparability for assessment of data quality.

Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. For data quality assessment procedures used to evaluate the completeness of data, see Section 8.1, Data Validation and Reporting.

Detection Limits

The sensitivity of any analytical method is related to the detection limits, the lowest concentration of analyte that can be detected at a specified confidence level. Definitions of Instrument Detection Limit, Method Detection Limit, Method Quantification Limit, and Practical Quantification Limit follow. The relationship of these terms is expressed graphically in Figure 3.

Instrument Detection Limit

Definition: The smallest signal above background noise that the instrument can detect reliably at 99 percent confidence level.

Measurement: Analyze replicate blank samples to determine the extent which the analyte signal exceeds the peak-to-peak noise.

Calculation: The mean value plus two standard deviations for a normal distribution or three for data distribution.

Method Detection Limit

Definition: The lowest possible concentration of a substance that can be identified, measured, and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing analyte.

Measurement: Analyze several replicates of a sample, digestate, or extracted sample with no detectable analyte to establish the estimated MDL. Prepare a concentration between three to five times the estimated MDL. Analyze seven aliquots and process each through the entire analytical method then calculate the standard deviation (S_d).

Calculation:

$$S_d = \sqrt{\frac{n\left(\sum x^2\right) - \left(\sum x\right)^2}{n(n-1)}}$$

$$MDL = 3.143(S_d)$$

The value 3.143 is from a table of the one-sided t distribution values where t = 6 degrees of freedom at the 99 percent confidence level.

Practical Quantification Limit

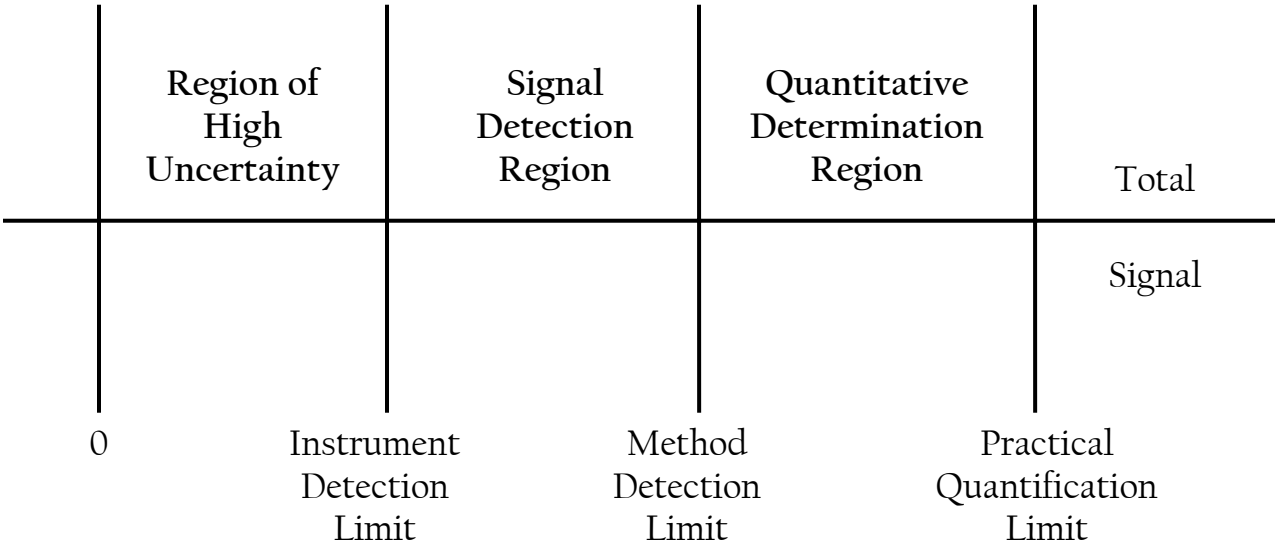
Definition: The minimum level that can be reliably achieved by the analytical method within specified limits of precision and accuracy during routine laboratory operating conditions.

Measurement: The PQL is 5 to 10 times the MDL.

Reporting Limits

The reporting limit is the PQL value of the specific analytical method. For specific reporting limits, see Appendix F.

Figure 3. Graphical Representation of Detection Limits



Relationships shown are not meant to indicate any absolute signal values.

13. Corrective Action

When errors, deficiencies, or out of control conditions are encountered, corrective actions are necessary. The need for corrective action may be identified in any number of ways:

- QC data outside acceptable limits for a given sample set
- Rising or falling trends that are detected in spike recovery or duplicate control charts
- Unacceptable levels of contamination in blanks and reagents
- Unusual changes in detection limits
- Calibration standards with low sensitivity
- Nonlinear or misshapen calibration curves
- Deficiencies detected by Laboratory QA Officer or senior staff reviewing analytical data
- Deficiencies detected during internal or external audits by Laboratory QA Officer, outside agency, or from performance evaluation studies

Since each analytical SOP has a QA section that outlines corrective actions to be taken, problems which may arise are usually handled at the analyst's level. If the problem persists and cannot be handled by the analyst, the matter is referred to the Laboratory QA Officer. The following corrective action steps are then taken:

- Identification of the problem
- Investigation and determination of the cause of the problem
- Corrective action determined to eliminate the problem
- Assigning responsibility for implementing corrective action
- Evaluation of the effectiveness of the corrective action
- Verification that the corrective action has eliminated the problem
- Documentation of the problem and corrective action needed

All suspect analytical results will be evaluated. The Laboratory QA Officer will not permit the analysis to go on-line until the corrective action has been completely successful. Corrective action documentation is routinely reviewed by the Laboratory QA Officer and Chief of the Bryte Chemical Laboratory for recurring problems which may require changes in analytical procedures, methods, or additional training of analysts.

14. Quality Assurance Reports

QA reports are generated by the Laboratory QA Officer with assistance form senior staff. These reports are used in evaluating the overall QA program, identifying problems and trends, and planning for future needs and requirements. These reports will usually include the following:

- All audit results including any necessary corrective action required
- Performance evaluation results and commentary
- Problems encountered and corrective action taken
- Any significant QA problems encountered
- Comments and recommendations

External reference samples from USGS, USEPA, DHS, or University of California, Davis are analyzed a minimum of three times per year. A QA report is generated after each external reference is completed. If special problems arise involving more than normal corrective action, a special QA report will be issued. The reports will be routed to specific staff members and finally, the Chief of the Bryte Chemical Laboratory.

15. Facilities and Laboratory Equipment

The Bryte Chemical Laboratory, located in West Sacramento, California contains a fully equipped 8,700 square foot facility. The fully air conditioned laboratory contains one large main room and smaller individual rooms with adequate hood area that is appropriately spaced with sufficient room to accommodate all personnel and equipment. The laboratory is divided into sections to handle the wide spectrum of chemical analyses performed on waters and wastewaters. The major sections consist of receiving, volatile organics, semi-volatile organics, trace metals, wet chemistry, nutrients, biological, and storage. Most of the instrumentation used in the chemical laboratory is fully automated and computerized (see Appendix H, Laboratory Equipment).

Appendix A
Water Sample Collection Information

Water Sample Collection Information

Determination	Method	Container	Sample Prep	Sample Size	Preservative	Hold Time
Alkalinity	SM 2320B	Polyethylene	Filtered	500 mL	4°C	14 days
BOD	EPA 405.1	Polyethylene	Unfiltered	2000 mL	4°C	48 hours
Carbamate Pesticides	EPA 531.1	Glass, Clear	Unfiltered	125 mL, teflon septa	4°C, chloroacetic Acid	28 days
COD	SM 5220A	Glass, Clear	Unfiltered	100 mL	4°C, H_2SO_4, pH<2	28 days
Chlorinated Pesticides	EPA 608	Glass, Amber	Unfiltered	1000 mL, teflon septa	4°C	7d ext, 40d after ext
Chlorinated Phenoxyacid Herbicides	EPA 615	Glass, Amber	Unfiltered	1000 mL, teflon septa	4°C	7d ext, 28d after ext
Chlorophyll	SM 10200H	Manila Envelope	Filtered	1000 mL	-20°C, dark	28 days
Chromium, hexavalent	EPA 218.6	Glass, Clear VOA	Unfiltered	40 mL	4°C	24 hours
Coliform, Fecal (Escherichia)	SM 9223 Colilert	Plastic, Sterile	Unfiltered	100 mL	4°C, $Na_2S_2O_3$	6 hours
Color	EPA 110.2	Polyethylene	Filtered	500 mL	4°C	48 hours
EDB/DBCP	EPA 504	Glass, Amber VOA	Unfiltered	40 mL x 2, teflon, no air	4°C, HCl, pH<2	28 days
Electrical Conductivity (EC)	SM 2510B	Polyethylene	Filtered	500 mL	4°C	28 days
Glyphosate	EPA 547	Glass, Amber	Unfiltered	125 mL, teflon septa	4°C	28 days
Haloacetic Acids (HAA)	EPA 552.2	Glass, Amber VOA	Unfiltered	40 mL x 2, teflon, no air	4°C	7d ext, 14d after ext
Haloacetic Acids Formation Potential (HAAFP)	EPA 510.1	Glass, Amber VOA	Filtered	40 mL x 3, teflon, no air	4°C	7d ext, 14d after ext
Hardness by Calculation	SM 2340B	Polyethylene	Filtered	250 mL	HNO_3, pH<2	6 months
Hardness, Total by Calculation	SM 2340B	Polyethylene	Unfiltered	250 mL	HNO_3, pH<2	6 months
ICP Cations, Dissolved – Na, Ca, Mg, K, B, Si	EPA 200.7	Polyethylene	Filtered	250 mL	HNO_3, pH<2	6 months
ICP Cations, Total – Na, Ca, Mg, K, B, Si	EPA 200.7	Polyethylene	Unfiltered	250 mL	HNO_3, pH<2	6 months
ICP/MS Trace Metals, Dissolved	EPA 200.8	Polyethylene, Acid Washed	Filtered	500 mL	HNO_3, pH<2	6 months
ICP/MS Trace Metals, Total	EPA 200.8	Polyethylene, Acid Washed	Unfiltered	500 mL	HNO_3, pH<2	6 months
IC Anions – Cl, SO_4, NO_3, Br, F	EPA 300.0	Polyethylene	Filtered	500 mL	4°C	28 days
Mercury by Cold Vapor	EPA 245.1	Polyethylene, Acid Washed	Unfiltered	500 mL	4°C, HNO_3, pH<2	28 days
Mercury by ICP/MS	EPA 200.8	Polyethylene, Acid Washed	Filtered	500 mL	4°C, HNO_3, pH<2	28 days

Water Sample Collection Information

Determination	Method	Container	Sample Prep	Sample Size	Preservative	Hold Time
Methylene Blue Active Substances (MBAS)	EPA 425.1	Polyethylene	Unfiltered	500 mL	4°C	48 hours
Nitrate, Nitrite (Nutrient)	SM 4500-NO_3-F	Polyethylene	Filtered	250 mL	-20°C, dark	48 hours
Nitrate, Nitrite (Nutrient DWR Modified)	SM 4500-NO_3-F DWR	Polyethylene	Filtered	250 mL	-20°C, dark	28 days
Nitrate, Nitrite (Std Mineral-IC Anions)	EPA 300.0	Polyethylene	Filtered	500 mL	4°C	48 hours
Nitrate, Nitrite (Std Mineral DWR Modified)	EPA 300.0 DWR	Polyethylene	Filtered	500 mL	4°C	28 days
Nitrogen/Phosphorus Pesticides	EPA 614	Glass, Amber	Unfiltered	1000 mL, teflon septa	4°C	7d ext, 40d after ext
Nitrogen, Ammonia	EPA 350.1	Polyethylene	Filtered	250 mL	-20°C, dark	28 days
Nitrogen, Kjedahl, Total (TKN)	EPA 351.2	Polyethylene	Unfiltered	250 mL	-20°C, dark	28 days
Nitrogen Organic, Dissolved (DON)	EPA 351.2	Polyethylene	Filtered	250 mL	4°C	28 days
Oil and Grease	EPA 1664	Glass	Unfiltered	1000 mL	4°C, H_3PO_4, pH<2	28 days
Organic Carbon Dissolved (DOC)	EPA 415.1 (D)	Glass, Clear VOA	Filtered	40 mL	4°C, H_3PO_4, pH<2	28 days
Organic Carbon Total (TOC)	EPA 415.1 (T)	Glass, Clear VOA	Unfiltered	40 mL	4°C, H_3PO_4, pH<2	28 days
Orthophosphate	SM 4500-P-F	Polyethylene	Filtered	250 mL	4°C	48 hours
Orthophosphate DWR Modified	SM 4500-P-F DWR	Polyethylene	Filtered	250 mL	-20°C, dark	28 days
pH	EPA 150.1	Polyethylene	Unfiltered	250 mL	4°C	15 minutes
Phosphorus Total	EPA 365.4	Polyethylene	Unfiltered	250 mL	-20°C, dark	28 days
Simulated Distribution System THM	SM 5710C SDS-THM	Glass, Amber VOA	Filtered	40 mL x 3, teflon, no air	4°C	7 days after FP
Simulated Distribution System HAA	SM 5710D SDS-HAA	Glass, Amber VOA	Filtered	40 mL x 3, teflon, no air	4°C	7d ext, 14d after ext
Solids, Settleable	EPA 160.5	Polyethylene	Unfiltered	2000 mL	4°C	7 days
Solids, Total Dissolved (TDS)	SM 2540C	Polyethylene	Filtered	500 mL	4°C	7 days
Solids, Total Suspended (TSS)	EPA 160.2	Polyethylene	Unfiltered	500 mL	4°C	7 days
Solids, Volatile Suspended (VSS)	EPA 160.4	Polyethylene	Unfiltered	500 mL	4°C	7 days
Trihalomethanes (THMS)	EPA 501.1	Glass, Amber VOA	Unfiltered	40 mL x 2, teflon, no air	4°C, HCl, pH<2	14 days
Trihalomethane Formation Potential (THMFP)	EPA 510.1	Glass, Amber VOA	Filtered	40 mL x 3, teflon, no air	4°C	7 days after FP
Turbidity	EPA 180.1	Polyethylene	Unfiltered	500 mL	4°C	48 hours
UVA	SM 5910B	Polyethylene	Filtered	250 mL	4°C	14 days
Volatile Organic Analysis (VOA)	EPA 502.2	Glass, Amber VOA	Unfiltered	40 mL x 2, teflon, no air	4°C, HCl, pH<2	14 days

Appendix B
Standard Operating Procedure

Analytical methods SOP must include:

1. Title
2. Scope and application
    - 2.1. Analytes
    - 2.2. Reporting limits
    - 2.3. Applicable matrices
    - 2.4. Calibration range
    - 2.5. Analysis time
3. Method Summary
4. Comments (interference or helpful hints)
5. Safety issues
6. Sample collection, preservation, containers, and holding times
7. Apparatus
8. Reagents and standards
9. Procedure
10. QA/QC requirements (QC samples, acceptance criteria, and corrective action)
11. Calculations
12. Reporting requirements (units, limits, significant figures, data entry)
13. References (method source, deviations from method source, and rationale for deviation)
14. Additional information as appropriate

Appendix C
Standard Labeling Requirements

A. Label must be written with waterproof ink

1. Directly on sample container
2. On gummed label
3. On attached sample tag

B. Label information requested when applicable

1. Sample number
2. Sample type (either by name or code number) i.e., metal, mineral, pesticide, biological, Code 7, etc.
3. Date sample collected
4. Location of sample
5. Filtered or unfiltered
6. Fixed (acidified)

C. Examples of label information used includes:

N04217	FQ03112	D08112
Nutrient	Metals	Method code 1
Unfilt.	Fixed & Filt.	Filtered
Clear Lake, Bot.	HMH2462, sump.	Bryte Bend
2/20/06	3/21/06	4/29/06

Appendix D
Precision and Data Accuracy

Precision – precision will be expressed in terms of RPD of the duplicate results from the original results. The equation for expressing precision is:

$$RPD = \frac{[A-B]\times 100}{\left(\frac{(A+B)}{2}\right)}$$

where RPD = Relative Percent Difference
A = First sample value
B = Second sample value (duplicate)

Accuracy – accuracy will be expressed in terms of spiked samples. Recovery of the spike will be used to assess the data accuracy. Recovery is calculated as follows:

$$Rec = \frac{(CD-D)x100}{C}$$

where Rec = Relative Percent Recovery
C = Amount of spike added
D = Sample concentration
CD = Value of sample with spike

Appendix E
Acceptable Quality Control Limits
Sample Matrix Spike

Determination	Control Limit %REC	RPD
MINERAL		
Alkalinity as $CaCO_3$ (titration)	78-116	20
pH	-	20
Specific Conductance (EC)	-	20
Dissolved Solids (TDS) @ 180	-	20
Turbidity	-	20
Silica as SiO_2 (ICP)	75-107	20
Nitrate (IC)	78-118	20
Boron (ICP)	79-112	20
Fluoride (IC)	85-117	20
Chloride (IC)	89-116	20
Sulfate (IC)	82-120	20
Calcium (ICP)	84-117	20
Magnesium (ICP)	86-113	20
Potassium (ICP)	82-108	20
Sodium (ICP)	82-116	20
Total Suspended Solids	-	20
Volatile Suspended Solids	-	20
Bromide (IC)	82-118	20
UVA (254nm UV abs.)	-	20
NUTRIENTS		
Total Kjedahl Nitrogen (automated, colorimetric)	74-127	30
Ammonia (automated, colorimetric)	86-118	20
(Nitrite + Nitrate) as N (automated, colorimetric)	79-119	20
Ortho-phosphate as P (automated, colorimetric)	83-112	20
Total phosphorus (automated, colorimetric)	70-124	30

Determination	Control Limit %REC	RPD
METALS-EPA 1638 (DISSOLVED)		
Aluminum	78-121	20
Arsenic	86-113	20
Cadmium	84-111	20
Chromium	86-108	20
Copper	84-107	20
Iron	76-121	20
Lead	80-106	20
Manganese	81-109	20
Nickel	84-106	20
Selenium	86-117	20
Silver	79-108	20
Zinc	86-110	20
METALS-EPA 1638 (TOTALS)		
Aluminum	81-119	20
Arsenic	89-112	20
Cadmium	87-109	20
Chromium	87-110	20
Copper	86-108	20
Iron	84-115	20
Lead	82-109	20
Manganese	82-112	20
Nickel	88-107	20
Selenium	89-115	20
Silver	87-105	20
Zinc	88-111	20

Determination	Control Limit %REC	RPD
METALS-EPA 200.8 (DISSOLVED)		
Aluminum	89-118	20
Antimony	86-110	20
Arsenic	87-110	20
Barium	80-112	20
Beryllium	77-123	20
Cadmium	87-109	20
Chromium	82-114	20
Cobalt	89-101	20
Copper	85-111	20
Iron	79-120	20
Lead	78-114	20
Manganese	80-116	20
Mercury	89-111	20
Molybdenum	84-107	20
Nickel	84-112	20
Selenium	87-112	20
Silver	80-111	20
Strontium	80-110	20
Thallium	94-106	20
Vanadium	87-115	20
Zinc	87-114	20
METALS EPA 200.8 (TOTALS)		
Aluminum	85-124	20
Antimony	91-104	20
Arsenic	90-105	20
Barium	80-111	20
Beryllium	81-120	20
Cadmium	91-104	20

Determination	Control Limit %REC	RPD
METALS EPA 200.8 (TOTALS)		
Chromium	85-111	20
Cobalt	84-109	20
Copper	88-107	20
Iron	80-124	20
Lead	85-107	20
Manganese	78-118	20
Molybdenum	88-109	20
Nickel	86-109	20
Selenium	85-110	20
Silver	89-104	20
Strontium	75-116	20
Thallium	87-105	20
Vanadium	86-111	20
Zinc	88-109	20
Mercury (Total) EPA 245.1	83-121	20
VOLATILE ORGANICS		
Benzene	86-108	20
Chlorobenzene	92-110	20
1,1-Dichloroethene	82-102	20
MTBE	86-112	20
Toluene	86-108	20
Trichloroethene	86-109	20
Chloroform	84-124	20
Chlorodibromoethane	84-106	20
Bromodichloroethane	78-111	20
Bromoform	94-116	20

Determination	Control Limit %REC	RPD
SEMIVOLATILE ORGANICS		
Aldicarb	73-128	30
Carbaryl	95-112	20
Oxamyl	87-121	30
Glyphosate	88-110	30
Cyanazine	63-84	30
Trifluralin	57-122	40
Aldrin	57-120	40
Lindane	65-119	40
Dieldrin	87-143	40
Heptachlor	84-132	40
2,4,5-T	106-133	40
2,4-D	94-112	20
Dicamba	89-127	30
Dichlorprop	76-110	30
MCPA	92-105	20

Notes:

1. List is not complete; as data becomes available, results will be entered.
2. Values listed are subject to change.
3. Limits were derived from surface, ground, and saline waters, and from agricultural wastewater.

Appendix F
Acceptable Quality Control Limits
Laboratory Control Samples

Determination	Control Limit %REC	RPD
MINERALS		
Calcium	85-125	20
Magnesium	85-125	20
Sodium	85-125	20
Potassium	85-125	20
Alkalinity	85-125	20
Sulfate	85-125	20
Chloride	85-125	20
Nitrate	85-125	20
Fluoride	85-125	20
Boron	85-125	20
Turbidity	85-125	20
Total Dissolved Solids	85-125	20
Specific Conductance	-	20
Silica	85-125	20
pH	85-125	20
Bromide	85-125	20
Suspended Solids	-	20
Volatile Suspended Solids	-	20
TOC	85-125	20
Oil and Grease	70-130	30
ORGANICS		
Volatile Organics (VOA, THM, EDB, DBCP)	80-120	20
Semivolatile Organics (OCP, OPP, NPP, HERB)	60-140	40
Carbamate, Glyphosate	70-130	30

Determination	Control Limit %REC	RPD
NUTRIENTS		
Total Phosphorus	70-130	30
Total Kjedahl Nitrogen	70-130	30
Dissolved ortho-phosphate as P	80-120	20
Dissolved (Nitrate + Nitrite) as N	80-120	20
METALS		
Aluminum	80-120	20
Antimony	80-120	20
Arsenic	80-120	20
Barium	80-120	20
Beryllium	80-120	20
Cadmium	80-120	20
Chromium	80-120	20
Cobalt	80-120	20
Copper	80-120	20
Iron	80-120	20
Lead	80-120	20
Lithium	80-120	20
Manganese	80-120	20
Mercury	80-120	20
Molybdenum	80-120	20
Nickel	80-120	20
Selenium	80-120	20
Silver	80-120	20
Strontium	80-120	20
Thallium	80-120	20
Vanadium	80-120	20
Zinc	80-120	20

Appendix G
Analytical Methods and Reporting Limits

Constituent		Method	Reporting Limit (mg/L)
MINERAL			
Calcium	EPA	200.7 ICP	1
Magnesium	EPA	200.7 ICP	1
Sodium	EPA	200.7 ICP	1
Potassium	EPA	200.7 ICP	0.5
Sulfate	EPA	300.0 Ion Chromatography	1
Chloride	EPA	300.0 Ion Chromatography	1
Nitrate	EPA	300.0 Ion Chromatography	0.1
Bromide	EPA	300.0 Ion Chromatography	0.01
Fluoride	EPA	300.0 Ion Chromatography	0.1
Boron	EPA	200.7 ICP	0.1
Silica	EPA	200.7 ICP	0.1
Total Dissolved Solids	Std Methods EPA	2540-C Gravimetric, Dried at 180°C 160.1 Gravimetric, Dried at 180°C	1 1
Alkalinity	Std Methods EPA	2320-B Titrimetric 310.1 Titrimetric	1 1
pH	Std Methods EPA	4500-H+ Electrometric 150.1 Electrometric	0.1 pH Unit 0.1 pH Unit
Specific Conductance	Std Methods EPA	2310-B Wheatstone Bridge 120.1 Wheatstone Bridge	1 umhos/cm 1 umhos/cm
Turbidity	Std Methods EPA	2130-B Nephelometric 180.1 Nephelometric	1 NTU 1 NTU
UV Absorbance	Std Methods	5910-B UV-Absorbing Organics	0.001 abs/cm at 254 nm

Constituent		Method	Reporting Limit (mg/L)
NUTRIENTS			
Ammonia	Std Methods	4500-NH_3 B, H Automated Phenate	0.01
	EPA	350.1 Automated Phenate	0.01
Total Kjedahl Nitrogen	EPA	351.2 Colorimetric, Semi-Automated	0.10
Nitrate*	Std Methods	4500-NO_3-F CD Reduction	0.01
	EPA	353.2 CD-Reduction, Automated	0.01
Nitrite*	Std Methods	4500-NO_3-F CD Reduction	0.01
	EPA	353.2 CD-Reduction, Automated	0.01
Nitrite + Nitrate*	EPA	353.2 CD-Reduction, Automated	0.01
o-Phosphate as P	Std Methods	4500-P-E Colorimetric, Ascorbic Acid	0.01
	EPA	365.1 Colorimetric, Ascorbic Acid	0.01
Phosphorus, Total	EPA	365.4 Colorimetric, Semi-Automated	0.01
METALS			
Aluminum	EPA	200.7 ICP	0.050
		200.8 ICP/MS	0.010
		1638	0.10 ug/L
Antimony	EPA	200.7 ICP	0.025
		200.8 ICP/MS	0.001
		1638	0.02 ug/L
Arsenic	EPA	200.7 ICP	0.010
		200.8 ICP/MS	0.001
		1638	0.10 ug/L
Barium	EPA	200.7 ICP	0.010
		200.8 ICP/MS	0.050
Beryllium	EPA	200.7 ICP	0.005
		200.8 ICP/MS	0.001
Cadmium	EPA	200.7 ICP	0.005
		200.8 ICP/MS	0.001
		1638	0.10 ug/L
Chromium (VI)	EPA	218.6 Ion Chromatography	0.005

* as N

Constituent		Method	Reporting Limit (mg/L)
Chromium (All valencies)	EPA	200.7 ICP 200.8 ICP/MS 1638	0.01 0.005 0.05 ug/L
Cobalt	EPA	200.7 ICP 200.8 ICP/MS	1 0.005
Copper	EPA	200.7 ICP 200.8 ICP/MS 1638	0.01 0.001 0.05 ug/L
Iron	EPA	200.7 ICP 200.8 ICP/MS 1638	0.01 0.005 0.10 ug/L
Lead	EPA	200.7 ICP 200.8 ICP/MS 1638	0.050 0.001 0.04 ug/L
Lithium	EPA	200.7 ICP 200.8 ICP/MS	0.01 0.005
Manganese	EPA	200.7 ICP 200.8 ICP/MS 1638	0.010 0.005 0.05 ug/L
Mercury	EPA	245.1 AA Flameless, Cold Vapor 200.8 ICP/MS	0.001 0.0002
Molybdenum	EPA	200.7 ICP 200.8 ICP/MS	0.01 0.005
Nickel	EPA	200.7 ICP 200.8 ICP/MS 1638	0.025 0.001 0.10 ug/L

Constituent		Method	Reporting Limit (mg/L)
Selenium	EPA	200.7 ICP 200.8 ICP/MS 1638	0.01 0.001 0.20 ug/L
Silver	EPA	200.7 ICP 200.8 ICP/MS 1638	0.01 0.001 0.03 ug/L
Strontium	EPA	200.7 ICP 200.8 ICP.MS	0.01 0.005
Thallium	EPA	200.7 ICP 200.8 ICP/MS 1638	0.10 0.001 0.02 ug/L
Vanadium	EPA	200.7 ICP 200.8 ICP/MS	0.01 0.005
Zinc	EPA	200.7 ICP 200.8 ICP/MS 1638	0.01 0.005 0.10 ug/L
MISCELLANEOUS			
Settleable Solids	Std Methods EPA	2540-F Volumetric, Imhoff 160.5 Volumetric, Imhoff	0.10 0.10
Suspended Solids	Std Methods EPA	2540-D, Gravimetric, 105°C 160.2 Gravimetric, 105°C	1 1
Color	Std Methods EPA	2120-D Visual Comparison, Pt-Co 110.2 Colorimetric, Pt-Co	5 Color Units 5 Color Units
Surfactants, MBAS	Std Methods EPA	5540-C Colorimetric 425.1 Colorimetric	0.10 0.10
COD (Chemical Oxygen Demand)	EPA	410.2 Titrimetric, low-level	1.0
Oil and Grease	Std Methods EPA	5520-B Gravimetric 1664 Gravimetric	5.0 5.0
BOD (Biological Oxygen Demand)	EPA	405.1 Incubation, 20°C	0.10

Constituent		Method	Reporting Limit (mg/L)
Organic Carbon (TOC)	Std Methods	5310-D Wet Oxidation, IR, Automated	0.50
	EPA	415.1 Wet Oxidation, IR, Automated	0.50
		415.1 Combustion, IR, Automated	0.50
Tannin & Lignin	Std Methods	5550-B Colorimetric	1
Volatile Suspended Solids	Std Methods	2540-E Gravimetric, 500°C	1
	EPA	160.4 Gravimetric, 500°C	1
ORGANICS			**(ug/L)**
Trihalomethane Potentials (THMFP)	EPA	510.1 (Modified) GC, Purge and Trap	1.0
1,2-Dibromoethane (EDB)	EPA	504 Gas Chromatography (GC)	0.02
1,2-Dibromo-3-Chloropropane (DBCP)	EPA	504 Gas Chromatography (GC)	0.01
Volatile Organics	EPA	502.2 Purge and Trap	0.5
Carbamates	EPA	531.1 High Pressure Liquid Chromatography (HPLC)	2.0-4.0
Glyphosate	EPA	547 HPLC	25.0
Haloacetic Acids	EPA	552.2 Gas Chromatography (GC)	1.0
Chlorinated Pesticides	EPA	608 Gas Chromatography (GC)	0.01-1.0
Nitrogen/Phosphorus Pesticides	EPA	614 Gas Chromatography (GC)	0.01-5.0
Chlorinated Phenoxy Acids (Herbicides)	EPA	615 Gas Chromatography (GC)	0.1-1.0

Appendix H
Laboratory Equipment

Organic Section	Quantity
Agilent 5973 GCMS with a PTV/LVI injector and split/splitless injector	1
Finnigan INCOS 50 GCMS with purge and trap and split/splitless capability	1
Varian 2200 Saturn Ion Trap GCMS with a Combipal SPME/PTV/LVI autosampler	1
Varian 2100 Saturn Ion Trap GCMS with purge and trap capability	1
Varain 8100 GC with dual ECD detectors	1
HP 5890 GC with dual ECD detectors	1
HP 5890 GC with dual ELCD detectors	1
HP 5890 GC with dual PID/ELCD detectors	1
Tekmar LSC 2000 purge and trap with an ALS 2016 autosampler	1
Tekmar LSC 3000 purge and trap with an ALS 2016 autosampler	1
Agilent 1100 HPLC with diode array and fluorescence detectors	1
Pickering Labs PCX 5200 post column derivatizer	1
Horizon 4970 SPE automated liquid solid phase extractor	1
OIC 1010 persulfate wet oxidation TOC analyzer with an OIC 1051 autosampler	1
OIC 1020A combustion TOC analyzer with an OIC 1051 autosampler	1
OIC 1030D wet oxidation/combustion TOC analyzer with an OIC 1051 autosampler	1
Inorganic Section	
Perkin Elmer ELAN 6000 ICP/MS DRC-e with a PE AS-91 autosampler	1
Perkin Elmer Optima 4300DV ICP with a PE AS-90 autosampler	1
Perkin Elmer 5000 AA spectrophotometer with a AS-91 autosampler	1
Varian Spectra 55 AA spectrophotometer with a SPS-5 sample prep station	1
Perkin Elmer Lambda 11 UV/VIS spectrophotometer with an autosampler	1
Technicon Auto Analyzer II segmented flow system with an autosampler	6
Lachat 8000 flow injection analyzer (FIA) with an XYZ autosampler	1

Inorganic Section (cont.)	Quantity
Thermo Konelab Aqua20 discrete analyzer with an autosampler	1
Braun & Luebbe Traccs 800 continuous flow system with an autosampler	1
Brinkmann Metrohm autotitrilyzer with a 712 conductometer, 719 titrator, and 745 autosampler	1
Fisher Scientific Model 400 computer aided autotitrimeter with a multisampler	1
Dionex DX500 ion chromatograph (IC) with an A540 autosampler	1
Dionex DX600 ion chromatograph (IC) with an A540 autosampler	1
Dionex DX4 ion chromatograph (IC) with a BioRad AS48 autosampler	1
Thermo Separation Products 3200 mercury analyzer with an autosampler	1
Bausch and Lomb Spectronic 88 UV/VIS spectrophotometer	1
Hach DR/4000U spectrophotometer	1
Hach 2100N turbidimeter	1
CEM Mars 5 microwave digestion unit	1
Thermo Orion 4 Star electroconductivity meter	1
Beckman sigma 63 pH meter	1
Fisher Scientific Accumet 25 pH/ion meter	2

Biological Section	
Perkin Elmer Lambda UV/VIS spectrophotometer	1
Colilert total and fecal coliform testing equipment – quanti-tray, sealer, incubator and UV lamp	1
Wild Heerbrugg inverted microscope with a Nikon camera attachment	1